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(54) Title: SHAPED ARTICLE WITH A CEMENT-BOUND MATRIX AND METHOD AND COMPOSITION FOR THE PREPARATION THEREOF (57) Abstract A shaped article comprising a cement-bound matrix with a low cement content, comprising: A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, such as ultrafine silica particles, the particles having an average size in the range of 0.002-2 µm; B) cement particles having an average size in the range of 2-7 µm; C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, such as fly ash particles, refractory bauxite particles, or metal particles, e.g. steel particles, the particles C having an average size in the range of 3-100 µm, the maximum size of the particles being 100 µm; D) a dispersing agent, such as a concrete superplasticizer (water reducing agent) in an amount of 0.1-4 % by weight of dry matter, calculated on the total weight of the particles A + B + C, the amount by volume of the particles B being in the range of 0.01-0.40 times the total volume of the particles B + C, the volume ratio of A based on the total volume of A + B + C being in the range of 0.10-0.40, and the volume concentration of A + B + C in the matrix being at least about 0.55, shows superior quality, such as superior compression strength and durability, compared to similar materials with larger cement particles.		

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FIELD OF THE INVENTION

Shaped article with a cement-bound matrix and method and composition for the preparation thereof

The present invention relates to improved inorganic binders

comprising a hydraulic cement, substantially inert fine particles, and ultrafine particles, which binders have a low proportion of

- 5 cement, to mortars and concretes having such binders as a binder matrix, to shaped articles comprising a matrix of such binders, to methods of preparing such articles, and to powder mixes for use in preparing the binders, mortars, concretes or articles.

BACKGROUND OF THE INVENTION

- 10 WO 80/00959, "Densified cement/ultrafine particle-based materials" (a paper presented by H.H. Bache at the Second International Conference on Superplasticizers in Concrete, Ottawa, Canada, June 10-12, 1981) and WO 81/03170 disclose a class of cement-based materials, the so-called "DSP materials", the binder matrix of which comprises
- 15 ultrafine particles (A) such as microsilica particles homogeneously arranged between densely packed particles (B) which are exclusively or predominantly cement particles. The dense and homogeneous structure is made possible by the use of an effective amount of a suitable dispersing agent such as a concrete superplasticizer. In
- 20 typical DSP materials, the binder is made from Portland cement and 10-40% by volume of ultrafine silica dust of an average particle size of about 0.1 μm , using 1-4% by weight of concrete superplasticizer, calculated as dry matter based on the combined weight of the cement and the silica dust, the ratio between the amount of water used in
- 25 the preparation of the binder and the combined amount of the cement and the silica dust being kept low to secure the dense structure. The DSP materials possess a number of desired qualities, such as high strength, high density (= very small porosity), and high durability, including high frost resistance.
- 30 After the publication of the above-mentioned references, a number of further developments in the field of DSP materials have been reported.

Thus, e.g., WO88/00575 discloses a method for the production of DSP materials in which cements which chemically are especially suitable are selected, or measures are taken to improve DSP materials when using cements which in themselves are chemically less suitable for the purpose.

JP 50657/1986 discloses DSP materials in which cement particles of an average size of 10.3 μm are used together with an inert inorganic powder and a superfine powder, the cement particles being used in proportions as low as 10%, to yield cast specimens which show high strengths.

JP 50659/1986 discloses cement-based materials comprising metal particles of a size of 1-100 μm which may replace up to 95% of the cement.

BRIEF DESCRIPTION OF THE INVENTION

It has now been found that the use of very small cement particles, that is cement particles having an average size in the range of 2-7 μm , in DSP binders with a low cement content results in materials which have markedly superior quality, e.g. strength and durability, compared to corresponding materials with larger cement particles. It has also been found that further pronounced advantages are obtained when these very small cement particles have a narrow particle size distribution. On the basis of this teaching, optionally combined with other measures as disclosed herein, a range of superior low cement products are provided.

Thus, in one aspect, the invention relates to a shaped article comprising a cement-bound matrix, the matrix comprising

A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, the particles having an average size in the range of 0.002-2 μm ,

B) cement particles having an average size in the range of 2-7 μm ,

C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, the particles C having an average size in the range of 3-100 μm , the maximum size of the particles being 100 μm ,

- 5 D) a dispersing agent in an amount of 0.1-4% by weight of dry matter, calculated on the total weight of the particles A+B+C,

the amount by volume of the particles B being in the range of 0.01-0.40 times the total volume of the particles B+C,

- 10 the volume ratio of A based on the total volume of A+B+C being in the range of 0.10-0.40, and

the volume concentration of A+B+C in the matrix being at least about 0.55.

In another aspect, the invention relates to powder compositions and liquid-containing compositions for producing such an article.

- 15 It is believed that the marked improvement in quality obtained by the use of the very fine cement particles in low cement binders of the DSP type containing ultrafine particles is related to transport paths during the solidification of the binder, i.e. the solidification of the dissolved "glue" material from the cement particles: The
- 20 structures are very dense, with ultrafine particles substantially homogeneously distributed throughout the interstices between the larger inert particles C. At the same time, the amount of cement available for delivering the "glue" is scarce, this being more pronounced the lower the cement content of the binder. Thus, it
- 25 seems most likely that the main reason for the improvement obtained according to the main aspect of the present invention is due to the more effective distribution of the scarce "glue" in the dense particle systems with ultrafine particles A in considerable concentrations, in which the possible pathways for the "glue" are
- 30 very narrow and limited. On the other hand, the surprising effect observed according to the present invention does not seem to be

merely an effect of the evidently better distribution of a finer material in a cement binder; experiments performed with low cement materials without ultrafine particles did not reveal any pronounced beneficial effect of using very fine cement particles.

5 DETAILED DESCRIPTION OF THE INVENTION

The expression "substantially inactive or less active than the particles B with respect to solidification of the matrix", as used about the particles A and the particles C in relation to the formation of the matrix, means that the material of which the particles C consist is not or is only to a very limited extent capable of delivering the chemical "glue" which "glues" the particles together to form a coherent matrix (by dissolution in the aqueous phase, chemical reactions and precipitation of reaction products). In the articles and compositions of the present invention, the "glue" is delivered predominantly by the cement particles.

By the term "average size" is meant the particle size at which 50% by weight of the particles are larger than the average size (and 50% by weight are smaller).

Examples of types of ultrafine particles A which may be used are alumina, calcium carbonate, calcium hydroxide, rice husk ash, metakaolin, oxides such as Al_2O_3 , SiO_2 , zirconium oxide and titanium oxide, and ground and/or sieved fly ash, quartz and slag. One important example of particles A is "microsilica", that is, silica rich ultrafine dust obtained as by-product in the production of ferrosilicium or silicon metal.

The cement may be any hydraulic cement, that is, a powder binder which hardens by reaction with water to form a product which is durable in water. The most important cements are Portland cement and aluminat cement. Examples of cements are normal Portland cement, high early strength Portland cement, sulfate resistant cement, low-alkali cement, low heat cement, white Portland cement, Portland blast furnace cement, Portland pozzolana cement, Portland fly ash

cement, and aluminate cement (high alumina cement). Especially preferred cements are white Portland cement and low-alkali cement.

The particles C may be any type of inorganic particle which fulfills the above conditions with respect to particle size and which do not to any substantial extent deliver the "glue" in the matrix formation. Examples of types of particles C which may be used are fly ash, fine quartz sand, slag, alumina, calcium carbonate and calcium carbonate-containing minerals such as dolomite and calcite, metakaolin, metal particles such as steel powder, and oxides such as Al_2O_3 , SiO_2 , zirconium oxide and titanium oxide. If desired, the particles C may advantageously be sorted, e.g. by sieving, so that the particles have a narrow particle size distribution. Special examples of particles C are especially strong mineral particles, e.g. the strong particles used in WO81/3170, such as calcined bauxite particles.

The dispersing agents selected should be able to substantially eliminate locking forces between particles in the mix and should have no negative effect with respect to the quality of the final structure. The dispersing agent is normally a concrete plasticizer, in particular a concrete superplasticizer, also called a water reducing agent or a high performance water reducing agent. Such agents are known to be effective with respect to rendering possible the distribution of ultrafine particles, such as ultrafine silica, between densely packed cement particles. By the use of concrete superplasticizers, such as a sodium salt of a highly condensed naphthalene sulphonc acid/formaldehyde condensate, of which typically more than 70% consists of molecules containing 7 or more naphthalene nuclei, it is easy to obtain an extremely good dispersion in a system combining the ultrafine particles A, the fine particles B and C and water, making possible the desired dense packing of the system in a low stress field. The amount of superplasticizer dry matter used is 0.1-4 percent, calculated on the total weight of the particles A, B and C. An alternative manner of expressing the amount of dispersing agent would be to refer it to the particles A and B solely. In this case, the amount of superplasticizer dry matter may be expressed as being 1-4 percent by weight, calculated on the weight of the ultrafine particles A and the cement particles B.

Although the present invention should not be limited to any theory, it is believed that one of the main reasons for the attainment of the remarkable improvements according to the invention resides in the construction of the binder with the ultrafine particles A arranged
5 densely and homogeneously and effectively bound together by cement delivered by the fine cement particles. This ultrafine system is then protected by a rigid "skeleton" formed by the larger particles, that is, the particles C and possibly to a certain extent the cement particles, this protection conferring toughness and stiffness to the
10 ultrafine structure. The cement particles B are very fine as stated above, and it is also preferred that very small particles C contribute to the building up of the skeleton.

However, the particles C (and preferably the particles B) should be large compared to the ultrafine particles, which means that the
15 particles C (and preferably the particles B) should preferably have an average size of at least 3 times the average size of the particles A, preferably at least 10 times the average size of the particles A, and more preferably at least 100 times the average size of the particles A. As will be explained in greater detail below, it is in
20 this connection, also very advantageous that the cement particles B, and the particles C, have a narrow particle size distribution, e.g. do not have any substantial particle size fraction approaching the size of the ultrafine particles, so that the particles B and C do not interfere with the packing of the particles A.

25 The density of the matrix should be high, as stated above at least a volume density of the particles A+B+C of 0.55. This is obtained in a manner known *per se*, by using an effective dispersing agent in a sufficient amount, and, quite generally, by using well-known measures to secure a dense and homogeneous structure, such as careful mixing
30 and securing that the matrix-forming materials are mutually compatible, which may be assessed, e.g., by a flow test as described in the examples. A high density of the binder secures that the particles B and C can arrange themselves so that they are in substantially direct particle-to-particle point contact to promote

the formation of strong inter-particle bonds between the particles of the protecting "skeleton".

In preferred binders of the invention, the volume concentration of the particles A+B+C in the matrix is at least 0.60, more preferably at least 0.70, and still more preferably at least 0.75.

As mentioned above, the content of the cement particles B is in the range from 0.01 to 0.40 by volume, calculated on the volume of the particles B+C. This means that the materials of the invention range from very high strength binders with cement contents in the range of 20-40% by volume, based on the volume of the particles B+C, via strong binders with a cement content in the range of 10-20% by volume, to materials having cement contents in the range from 10% by volume down to extremely low contents such as 6%, 3%, 1.5% and even 1% by volume, based on the volume of the particles B+C. Due to the use of the special fine cement particles B, in particular with a narrow particle size distribution as discussed below, such materials can be made with a surprisingly high quality using normal mixing and casting techniques, and with an even higher quality using special mixing techniques employing vibration and pressure compaction, such as explained below. Furthermore, other types of concrete superplasticizers, for example melamine based concrete superplasticizers, e.g. Sikament®-FF, may also be employed.

It will be understood that the binder matrix according to the invention will normally be combined with additional bodies, such as sand to make a mortar, or sand and stone to make a concrete, and that mortars or concretes according to the invention can be reinforced using e.g. steel bars, mesh or wire. Also, due to the high quality of the binder, it is very well suited for being reinforced with fine fibres, whiskers, etc.

The high strength shaped binder compositions according to the invention are advantageous for use in, e.g., structural concrete, such as for buildings, bridges and roads, because of their beneficial properties such as very high strength, stiffness and durability, low permeability, increased volume stability, reduced creep, reduced

hydration shrinkage and drying shrinkage, and reduced heat development during hydration, as compared with conventional high quality concretes.

- Compared to DSP materials with higher cement contents, the compositions according to the invention may be advantageous for one or more of the same reasons as stated above, and for purposes where a high concentration of particles C is desirable, such as where the particles C are particles conferring wear resistance, the compositions of the invention will be especially advantageous.
- 10 The compositions according to the invention with very low cement contents are of particular interest when the cement content *per se* should be kept as low as possible, e.g. for low cement castables which are to be converted into ceramic type materials by heating or firing. For such castables, the compositions according to the
- 15 invention are advantageous because of high density, reduced sintering contraction, and higher refractoriness, that is, higher working temperatures, due to the reduced cement content. In a particular aspect, it is even contemplated that Portland cement, such as low alkali cement or white Portland cement, can be used as the
- 20 cement in low cement castables according to the invention, due to the very low amount of cement necessary according to the present invention.

The average size of the cement particles is preferably in the range of 2-5 μm , often more preferably in the range of 2-3 μm .

- 25 According to a specially advantageous embodiment of the invention, the cement particles, in addition to being very fine as defined above, have a narrow particle size distribution with the ratio D_{90}/D_{10} of at the most about 12. [The ratio D_{90}/D_{10} is the ratio between the diameter (D_{90}) at which 90% by weight of the particles
- 30 have a smaller diameter and the diameter (D_{10}) at which 10% by weight of the particles have a smaller diameter. Corresponding designations of other ratios herein are defined analogously.]. In principle, the particle size distribution should be as narrow as

possible, and very desirable values D_{90}/D_{10} for the cement particles are in the range of 3-10, in particular 3-7 and more preferred 3-5.

According to a further preferred embodiment, the cement particles should preferably have as little content of very fine particles as possible, as the very fine cement particles may disturb the packing of the ultrafine particles A and/or may dissolve completely in the mix water and cause undesired early hardening phenomena which can disturb the attainment of an optimum homogeneity in the fine particle system. For this reason, it is preferred that the ratio D_{10}/D_5 of the cement particles, (that is, in accordance with the explanation given above, the ratio between the diameter (D_{10}) at which 10% by weight of the particles have a smaller diameter and the diameter (D_5) at which 5% by weight of the particles have a smaller diameter) is at the most 1.5.

As appears from the examples, great additional advantages are obtained when the cement particles have a narrow particle size distribution as defined above and have a very small content of very fine particles. Such cement particles are easier to incorporate into the mixes with attainment of maximum density, and apart from giving rise to a higher quality of the resulting shaped articles, they also give advantages during the production of the articles, such as a longer pot life and a lower requirement for the amount of dispersing agent.

It is preferred that the particles A have an average size in the range of 0.03-1 μm , in particular an average size of about 0.1-0.5 μm . The particles A used in the examples have an average particle size in this range.

The particles A are preferably spherical particles. A relatively broad particle size distribution of the particles A will give the most dense packing under ideal conditions, but this may in certain cases be counteracted because of increasing difficulties in the homogeneous arrangement of the particles, the finer the particles are. For this reason, in a special embodiment of the invention, it is preferred that also the particles A have a narrow particle size

distribution, such as a particle size distribution with the ratio D_{90}/D_{10} of at the most about 20, preferably at the most about 10, more preferably at the most about 5. In a very special embodiment of the invention, the particles A comprise two particle size fractions, such as one in the range of 0.5-1 μm and another one in the range of 0.05-0.1 μm , preferably with one or both of the fractions being narrowly graded as mentioned above.

Interesting particles C are particles having an average size in the range of 50-100 μm , or particles having an average size in the range of 2-40 μm , in particular 2-20 μm , e.g. 2-10 μm and as small as 2-5 μm . It is especially valuable to have larger particles C which have a narrow size distribution with the ratio D_{90}/D_{10} of at the most about 10, preferably of at the most about 6.

In a preferred embodiment, the particles C comprise two fractions with gap grading, one fraction having an average size in the range of 50-100 μm and the other fraction having an average size in the range of 2-10 μm . It is especially preferred that at least one of the particle C fractions has a narrow particle size distribution, the ratio D_{90}/D_{10} of the fraction having an average size in the range of 50-100 μm being at the most 4, and/or the ratio D_{90}/D_{10} of the fraction having an average size in the range of 2-10 μm being at the most about 8. All of these measures contribute to improving the density and quality of the binder and the processing conditions, corresponding to what is explained above.

It is particularly preferred that the particles C are substantially spherical.

The invention also relates to a powder composition for use in producing a binder matrix according to the invention, or, expressed in another manner, for use in producing a shaped article according to the invention. The powder composition may be one which contains the ultrafine particles, the cement, and the particles C, and optionally sand, and to which water and the dispersing agent are added to form a mix, or it may be one which additionally contains the dispersing agent, and to which only water is to be added to form a mix. In both

cases, the types and amounts of the constituents and, with respect to the particles, their particle sizes and particle size distributions, can suitably be adapted in accordance with the above discussion.

Special powder compositions according to the invention are
5 compositions which do not contain cement particles B, but which contain the very special combination of particles A and particles C which comprise two particle size fractions with gap grading as explained above, the particles preferably being spherical, in particular where at least one of the particle C fractions has a
10 narrow particle size distribution as explained above.

Furthermore, the invention relates to a fluid composition for use in making a shaped article, the fluid composition either comprising all of the essential constituents for making the binder, that is, the particles A, the cement particles B, the particles C, the dispersing
15 agent, and water, or comprising, e.g., the constituents except the cement, or the constituents without the cement and without the dispersing agent, so that the appropriate amount of cement and an adapted amount of dispersing agent is added to form the final mix. In both latter cases, the particles C will be the special particles
20 comprising two particle size fractions with gap grading, and optionally with a narrow particle size distribution in one or both fractions. In the fluid composition, the amount of water should be kept sufficiently low to allow the attainment of the desired particle concentration in the resulting matrix made from the composition.

25 The production of shaped articles according to the present invention may be performed in accordance with normal mixing and casting techniques as known, e.g., for DSP materials, aimed at arranging the particles in a homogeneous and dense system, that is, with sufficient mixing and sufficiently long mixing times to obtain a well saturated
30 homogeneous dense system. Such methods and additional methods which employ pre-mixing of the finest components and subsequent addition of the somewhat larger particles are described in the Examples. In many cases, it will be preferred that the curing is performed without any initial heating, so as to make it possible for the small amount of
35 cement to diffuse throughout the ultrafine structure before any

substantial hardening takes place, but it is also possible to utilize heat curing and other curing regimens known to increase the strength of conventional cement-bound materials.

As will be understood, the components of the particle system should
5 be compatible from a chemical and surface chemical point of view, in particular, the particles A, the cement particles, and the dispersing agent should be selected so that they will be compatible with each other. Thus, e.g., W088/00575 discloses that the cement and the particles A should be selected and/or the mix adapted so that the
10 content of water-soluble alkali in the mix originating from the mineral solids in the mix is at the most 0.30%, calculated as Na_2O equivalents, relative to the weight of the cement in the mix.

EXAMPLES

MATERIALS AND METHODS

In the following, a general description is given of the materials and methods used in Examples 1-13.

- 5 The following table provides a summary of the materials used in Examples 1-13:

	Ingredients	Example				
		1	2	3	4	5
10	White cement	+				
	Very fine white cement I		+	+	+	+
	Fly ash II	+	+		+	+
	Fine fly ash					+
	Fine quartz			+		
15	Microsilica II	+	+	+	+	+
	Flube	+	+	+	+	+
	Water	+	+	+	+	+
	Sand 0-0.25 mm	+	+	+	+	+
	Sand 0.25-1.0 mm	+	+	+	+	+
20	Sand 1.0-4.0 mm	+	+	+		+
	Stone 5-8 mm				+	
	Stone 8-11 mm				+	

	Ingredients	Example							
		6	7	8	9	10	11	12	13
	White cement	+							
5	Very fine white cement II	+	+			+	+		+
	Air-classified fine white cement							+	+
	High alumina cement			+					
10	Fine high alumina cement				+				
	Fly ash III	+		+	+	+	+		
	Air-classified fly ash							+	
	Microsilica II	+	+	+	+	+	+	+	+
15	Flube	+	+	+	+	+	+	+	+
	Water	+	+	+	+	+	+	+	
	Sieved fine sand						+	+	
	Sæby sand 0-0.25 mm								+
	Steel powder		+						
20	Sand 0-0.25 mm					+			+
	Sand 0.25-1 mm					+		+	+
	Sand 1-4 mm							+	+
	Stone 5-8 mm					+			
	Stone 8-11 mm					+			
25	Bauxite 0-1 mm	+	+	+	+				
	Bauxite 1-4 mm	+	+	+	+				

Cement

30 In examples 1-7, a white Portland cement (density 3150 kg/m³, Blaine surface 411 m²/kg) is employed. The grain size distribution of the white Portland cement used in Example 1 is as follows:

15

	%< 50 μm	99.0
	%< 20 μm	88.0
	%< 10 μm	47.0
	%< 5 μm	25.0
5	%< 2 μm	10.0
	%< 1 μm	4.0

For use in Examples 2-7, the white Portland cement (very fine white cement I) is finely ground, with a Blaine surface of 757 m^2/kg , a BET surface of 2950 m^2/kg and the following particle size distribution:

10	%< 63 μm	99.58
	%< 50 μm	99.0
	%< 20 μm	97.0
	%< 10 μm	79.0
	%< 5 μm	47.0
15	%< 2 μm	21.0
	%< 1 μm	8.0
	%< 0.5 μm	1.0

The density of the Portland cement used in these examples is 3171 kg/m^3 .

- 20 The white Portland cement of Examples 6 and 7 has the following chemical composition (% by weight):

	SiO_2	24.3
	Al_2O_3	1.84
	Fe_2O_3	0.31
25	CaO	69.12
	MgO	0.56
	Free CaO	2.70
	SO_3	2.14
	Loss on ignition	0.69
30	K_2O	0.04
	Na_2O	0.11
	$\text{Na}_2\text{O eq.}$	0.136

In Example 8, an aluminous cement (Alcoa CA-14) with a density of 2999 kg/m³ and the following chemical composition (% by weight) was employed:

	SiO ₂	6.28
5	Al ₂ O ₃	63.92
	Fe ₂ O ₃	0.07
	CaO	27.48
	MgO	0.11
	SO ₃	0.01
10	Loss on ignition	0.17
	K ₂ O	0.03
	Na ₂ O	0.32
	Na ₂ O eq.	0.34
	TiO ₂	0.02

15 The aluminous cement had the following particle size distribution:

	%< 50 μ m	94
	%< 20 μ m	59
	%< 10 μ m	35
	%< 5 μ m	19
20	%< 2 μ m	6
	%< 1 μ m	1

In Example 9, the aluminous cement was finely ground and had the following particle size distribution:

	%< 50 μ m	100
25	%< 20 μ m	91
	%< 10 μ m	64
	%< 5 μ m	41
	%< 2 μ m	19
	%< 1 μ m	9

30 In Example 13, a finely ground white Portland cement (very fine white cement II) having the following grain size distribution was employed:

	%< 50 μm	98
	%< 20 μm	92
	%< 10 μm	77
	%< 5 μm	50
5	%< 2 μm	25
	%< 1 μm	13
	%< 0.5 μm	5
	%< 0.3 μm	1.5

10 In Example 12, an air-classified white Portland cement (obtained by sorting the cement using an air stream) was employed. Substantially all of the particles of the air-classified white Portland cement had a size of between 2 and 10 μm . The particle size distribution was as follows:

	%< 10 μm	97
15	%< 8 μm	90
	%< 7 μm	82
	%< 5 μm	55
	%< 3 μm	15
	%< 2 μm	5
20	%< 1 μm	1

Fly ash

In Examples 1, 2, 4, and 5, a fly ash (Fly ash II, density 2280 kg/m^3) with the following chemical composition is employed:

	SiO ₂	55.10
	Al ₂ O ₃	22.43
	Fe ₂ O ₃	9.60
	CaO	3.55
5	MgO	2.12
	SO ₃	0.70
	Loss on ignition	2.32
	K ₂ O	2.03
	Na ₂ O	0.88
10	Na ₂ O eq.	2.22

Fly ash II has the following grain size composition:

	%< 63 μ m	85.2
	%< 50 μ m	74.0
	%< 20 μ m	51.0
15	%< 10 μ m	29.0
	%< 5 μ m	12.0
	%< 2 μ m	1.0
	%< 1 μ m	0.0

20 In Example 5, a finely ground fly ash was employed by grinding of the above-mentioned fly ash II. This fine fly ash had a density of 2717 kg/m³ and a particle size distribution as follows:

	%< 50 μ m	98
	%< 20 μ m	91
	%< 10 μ m	76
25	%< 5 μ m	53
	%< 2 μ m	21
	%< 1 μ m	12
	%< 0.5 μ m	7

30 In Examples 6, 8 and 9, a fly ash (Fly ash III) with the following grain size distribution and chemical composition is employed:

	%<200 μm	99.3
	%< 90 μm	93.7
	%< 63 μm	89.3
	%< 50 μm	84.0
5	%< 20 μm	62.0
	%< 10 μm	38.0
	%< 5 μm	17.0
	%< 2 μm	3.0

	SiO_2	53.46
10	Al_2O_3	21.82
	Fe_2O_3	8.78
	CaO	4.90
	MgO	2.69
	SO_3	1.01
15	Loss on ignition	2.63
	K_2O	2.12
	Na_2O	0.87
	$\text{Na}_2\text{O eq.}$	2.26

20 The fly ash used in Examples 10 and 11 corresponds substantially to fly ash III.

Air-classified fly ash

In Example 12, a fly ash with a narrow grain size distribution (obtained by sorting the fly ash using an air stream) was employed. The air-classified fly ash had an average particle size of about 6.5 μm and the following grain size distribution:

	%< 50 μm	99
	%< 20 μm	96
	%< 10 μm	81
	%< 5 μm	32
30	%< 2 μm	1

Fine quartz

In Example 3, finely ground quartz with the following grain size distribution is employed:

	%< 63 μm	99.31
5	%< 50 μm	99.3
	%< 20 μm	86.0
	%< 10 μm	56.0
	%< 5 μm	36.0
	%< 2 μm	19.0
10	%< 1 μm	12.0

Sæby sand 0-0.25 mm

In Example 13, a relatively fine sand (Sæby sand) having a grain size of 0-0.25 mm and the following grain size distribution was employed:

	%< 2 mm	100
15	%< 1 mm	96
	%< 0.5 mm	94
	%< 0.25 mm	89
	%< 0.125 mm	57
	%< 0.090 mm	36
20	%< 0.038 mm	4

Sieved fine Sæby sand

In Examples 11 and 12, the above mentioned Sæby sand is sieved and the fine fraction (0-0.25 mm) employed. The sieved fine Sæby sand has a density of about 2600 kg/m³ and the following grain size distribution:

	%< 0.125 mm	100
	%< 0.090 mm	63
	%< 0.063 mm	26
	%< 0.038 mm	7

Microsilica

Microsilica (microsilica II, density 2220 kg/m³, specific surface (BET) 21,400 m²/kg) with the following chemical composition is used:

5	SiO ₂	84.92
	Al ₂ O ₃	1.30
	Fe ₂ O ₃	3.25
	CaO	0.48
	MgO	1.32
10	SO ₃	0.75
	Loss on ignition	3.32
	K ₂ O	2.81
	Na ₂ O	0.93
	Na ₂ O eq.	2.78

15 *Sand, stone and bauxite*

The employed quartz sand and stone (hyperite) had the following characteristics:

		Density (kg/m ³)	Water absorption (%)
20	0-0.25 mm sand	2628	0.4
	0.25-1 mm sand	2638	0.3
	1-4 mm sand	2606	0.7
	5-8 mm stone	3052	0.5
	8-11 mm stone	3070	0.5
25	11-16 mm stone	3084	0.4

The particle size distribution for the fine sand (0-0.25 mm) was as follows:

	%< 0.500 mm	99
	%< 0.250 mm	93
	%< 0.125 mm	28
	%< 0.090 mm	4
5	%< 0.075 mm	4
	%< 0.063 mm	2

In Examples 6 and 7, bauxite is employed instead of sand. The 0-1 mm bauxite fraction has a density of 3.475 g/cm³ and the following size distribution:

10	%< 1 mm	99.3
	%< 0.5 mm	60.5
	%< 0.25 mm	30.4
	%< 0.125 mm	11.2

The 1-4 mm bauxite fraction has a density of 3.297 g/cm³ and the following size distribution:

	%< 4 mm	100
	%< 2 mm	55.4
	%< 1 mm	6.4
	%< 0.5 mm	0.5

20 *Dispersing agent and water*

As a dispersing agent, a concrete super-plasticizer with the trade name "Flube" was used. Flube is a sodium salt of a highly condensed naphthalene sulphonic acid/formaldehyde condensate, with an estimated powder density, referring to the density when dissolved in water, of 1600 kg/m³. The water employed was common tap water.

Mixing

Two types of materials were prepared: mortar having a maximum particle size of less than 4 mm and concrete containing particles larger than 4 mm and having a maximum particle size of either 11 mm or 16 mm. In preparing concrete, the mortar portion was prepared first, after which the stone was added, so that the mixing of the mortar was the same regardless of whether the mortar was used alone or together with the stone to form a concrete.

Except as otherwise noted, mixing generally was carried out as follows: Mixing of the mortars took place in a 20 l paddle mixer (for the preparation of mortar samples) or in a 50 l paddle mixer (Eirich) (for the preparation of mortars to be used in concrete). The dry materials, i.e. all the materials except water, were first mixed for one minute, after which the water was added while the mixer rotated. The addition of water took about 10-20 seconds. Mixing was then continued for 10 minutes (in certain cases somewhat longer).

During the mixing after addition of water, the consistency was in the beginning dry and the colour was light, but afterwards the mass gradually acquired a darker colour and a moist consistency, whereby a plastic and more homogeneous material was gradually obtained, the material finally becoming a more fluid homogeneous mass.

After mixing, the mortars' consistency was determined by flow table measurements according to the ASTM flow table measurement technique (ASTM C230-83). With this technique, the diameter of a mortar sample is measured first prior to impact and subsequently after impact performed by letting the mortar sample fall a distance of about 12.7 mm 20 times according to the following procedure: the flow table is dried and the mould (height 50 mm) for casting the flow specimen is placed in the center of the table. A layer of mortar, about 25 mm thick, is placed in the mould using a spoon. The layer is stamped 20 times with a stamper. The stamper pressure is adjusted so that the mould is uniformly filled. The mould is filled entirely with mortar and stamped as above (20 times). The mould should at least be filled. Excess material is scraped off so that the surface of the mortar is

even with the top of the mould. Any mortar which may have been spilled is wiped off. The mould is removed 1 minute after mixing is completed. The static flow table measurement is made 20-30 seconds after the mould is removed and the dynamic flow table measurement is
5 made after impact 20 times from a height of 12.7 mm.

Mixing of concrete

Mixing of concrete took place after premixing of the mortar (in a 50 l mixer) as described above, after which stone was added and mixing was carried out for 5 minutes. The consistency of the mixes
10 was moist and the structure was open with a thin layer of mortar being attached to the surface of the stones. After subsequent compaction by vibration as described below, the mass became homogeneous and coherent.

Casting of samples

15 Series of samples were cast, primarily as cylinders with a length of 200 mm and a diameter of 100 mm. Most of the samples were cast on a vibrator table at a relatively low effect at a frequency of 50 cycles/sec. and an amplitude of 0.44 mm (peak to peak 0.88 mm). A few of the samples were prepared on a vibrator table with a greater
20 effect working at a frequency of about 150 cycles/sec. and an amplitude of 0.3 mm. The preparation of samples on the 50 cycles/sec. vibrator table was accomplished by filling the mix in cylindrical molds in 4-5 portions over a period of 1 to 2 minutes. The materials (the mortars) flowed well under the vibration. To avoid excessive
25 swelling of the material during vibration (a resonance phenomenon which often occurs during vibratory compaction of soft materials in an open mold, especially fine grained materials), a steel rod with cross-sectional dimensions of 3 x 3 cm was used as a counterweight. After filling, the molds were closed by fastening a lid on the
30 cylinders.

The preparation of samples on the 150 cycles/sec. vibrator table was accomplished with vibration under combined static and dynamic pressure, established with a steel cylinder (weight 8 kg) placed on top of the material during vibration. The samples were cast by
5 pouring the mix in 4 to 5 portions over a period of 1 to 2 minutes. After filling, the molds were closed as described above.

Hardening/curing

A series of different hardening procedures were used.

Hardening at 80°C

10 The cast samples in the sealed molds were placed in water having a temperature of 80°C within 1 to 2 hours after casting. The samples were removed from the hot water after 24 hours and placed (still in the sealed molds) in air having a temperature of 20°C for approximately 24 hours, after which the molds were removed and the
15 samples were kept in air (20°C, approx. 70% relative humidity) until they were tested for strength, which normally occurred within one week.

Hardening at 20°C

The cast and sealed samples were kept for 24 hours at 20°C (covered
20 by wet towels and sealed in plastic), after which the molds were removed and the samples were placed in water with a temperature of 20°C for extended hardening. Some of these samples were tested for strength immediately after curing in water. Others were kept for 5 to 7 days at a temperature of 45°C in air before testing for strength.

25 All of the samples were weighed after removal from the molds as well as at later stages.

Density

The density of the samples was determined by weighing the samples out of and in water at a temperature of 20°C, the density of the water being assumed to be 1000 kg/m³. The measured values for density were
5 in many cases compared with the density of the materials, calculated on the basis of the mix compositions and the densities of the individual ingredients, under the assumption that the materials were "perfectly" compacted without the presence of voids (air). These values are referred to as the "theoretical densities".

10 *Sound velocity and dynamic modulus of elasticity*

The sound velocity in the materials was determined (for high frequency low energy waves) by measuring the time it took an impulse to travel through the sample (20 cm for cylinders).

On the basis of density (ρ) and the sound velocity (v), the dynamic
15 modulus of elasticity may be calculated as follows:

$$E = \rho v^2$$

where E refers to high frequency low energy performance.

Compressive strength

The compressive strength of the materials was determined in oil
20 pressure driven presses, using either a 600 t press or a 500 t press. The applied stresses increased at a constant rate of 0.8 MPa/sec.

Packing of dry materials

In order to characterize the packing of different types of coarser
25 particles, the degree of packing of dry sand and stone in open containers was determined. The results are given below, in which the upper number is after simple pouring of the dry materials, and the

lower number is after vibration on a vibrator table using a vibration of 50 cycles/sec. for about 15 seconds. The sand was packed in a 3 litre container and the stone was packed in a 1 litre container.

Particle grading

- 5 The following values and ratios regarding the particle sizes of a number of the materials used in the examples were determined:

		Example No.	D ₉₀	D ₅₀	D ₁₀	D ₅	$\frac{D_{90}}{D_{10}}$	$\frac{D_{10}}{D_5}$
10	Air-classified white cement	12	8	4.8	2.6	2.0	3.1	1.3
	Very fine white cement I	2,3, 4,5	12	5.4	1.1	0.74	11.4	1.5
15	Very fine white cement II	6,7, 13	16	5.0	0.82	0.5	19.5	1.6
	White cement	1,10, 11,13	23	10.5	1.95	1.1	11.8	1.8
20	High alumina cement	8	43	16	2.8	1.7	15.4	1.6
	Fine high alu- mina cement	9	19	6.7	1.1	0.65	17.3	1.7
25	Air-classified fly ash	12	12.5	6.4	3.15	2.65	4.0	1.2

EXAMPLE 1

Reference example, mortars containing cement with average particle size 10.5 μm

Three mortars, C-25%, C-12.5% and C-6%, containing binders with silica fume and different contents of cement and fly ash, were prepared. A relatively large binder content in the mortars of 47% by volume was employed in order to test the binder, since the normal binder content in such materials is typically about 20-30%. The mortars are referred to according to the cement content by volume based on the content of cement in a mix C-100%, which contains no fly ash.

The binders comprised white Portland cement as the active particles, fly ash and microsilica. The data of the materials appear from "Materials and Methods". The average particle size of the cement was 10.5 μm ; the ratio D_{90}/D_{10} was 11.8, and the ratio D_{10}/D_5 was 1.8.

The mix compositions were as follows:

		g per approx. 10 l mortar			
		C-100%	C-25%	C-12.5%	C-6%
20	White cement	7730	1935	965	465
	Silica	1845	1845	1845	1845
	Fly ash	0	4085	4765	5121
	Flube	235	235	235	235
	Sand 0-0.25 mm	1980	1980	1980	1980
25	Sand 0.25-1 mm	3945	3945	3945	3945
	Sand 1-4 mm	7895	7895	7895	7895
	Water	1285	1285	1285	1285

The consistency of the mixed materials prior to casting was determined by flow table measurements as described above. The results are as follows, the upper number giving the diameter (cm) before impact and the lower number giving the diameter after impact:

Mortar type	C-100%	C-25%	C-12.5%	C-6%
Before	-	13.3	15.0	17.0
After	13.9	16.7	19.5	21.2

5

It was determined as described above in "Materials and methods" that the packing density of the fine particles (cement + fly ash) was about 0.52 and that the total density of the cement, fly ash and
10 microsilica was about 0.69.

Samples were prepared in the form of cylinders (diameter 100 mm, height 200 mm) by casting in an open mold using gentle vibration. The procedure for mixing and casting was as described above in "Materials and Methods". Four cylinders were prepared from each type of mortar.
15 The cylinders were hardened in sealed molds for 2 days, the first 24 hours in hot (80°C) water, and then in 20°C air, after which the samples were removed from the molds and kept in air with a temperature of 20°C. Three of the four cylinders from each type of mortar were tested for compressive strength five days after the
20 samples were removed from the molds. The remaining cylinders (one from each type of mortar) were used for supplementary investigations. Immediately following removal from the molds, all cylinders were weighed (in and out of water) and sound velocity through the samples was determined.

25 Density, sound velocity, dynamic modulus of elasticity and compressive strength were determined as described above. The results are summarized in the following table, in which the compressive strength is an average of 3 samples and the other determinations an average of 4 samples:

	Mortar	C-100%	C-25%	C-12.5%	C-6%
	Density (kg/m ³)	2471 (2.5)	2316 (12.5)	2290 (2.9)	2269 (2.0)
5	Sound velocity (m/sec)	5586 (31)	5076 (47)	4717 (42)	4226 (33)
	Dynamic modulus of elasticity (MPa)	77,111 (852)	59,705 (1373)	50,955 (889)	40,525 (648)
10	Compressive strength (MPa)	*	136.5 (1.3)	85.2 (4.6)	38.8 (0.35)

* No average is given; the individual values were 126.5, 201.6 and 177.1 MPa. The true strength of the material is most likely best represented by the largest value.

15

EXAMPLE 2

Mortars according to the invention, containing finely ground cement with average particle size 5.4 μm

20 The effect of using particularly fine ground cement in two mortars with a very low cement content was investigated.

25 The mortars were equivalent to the mortars C-12.5% and C-6% used in the Example 1, with the exception that the cement in Example 1 was replaced by a very finely ground cement having an identical chemical composition to that of the cement of the Example 1. The data of this cement appear from "Materials and Methods". The average particle size of the cement was 5.4 μm ; the ratio D_{90}/D_{10} was 11.4, and the ratio D_{10}/D_5 was 1.5.

The mix compositions are shown in the following table:

Mixture	I	II
	C-12.5%	C-6.0%
White cement*	965	465
5 Microsilica	1845	1845
Fly ash	4765	5121
Flube	235	235
Sand 0-0.25 mm	1980	1980
Sand 0.25-1 mm	3945	3945
10 Sand 1-4 mm	7895	7895
Water	1285	1285

* Finely ground

The procedure was also the same as that of Example 1. The two materials flowed easily and the flow properties of the two mixtures were apparently the same.

Flow table measurements for the mixtures gave the following results:

Mixture	12.5% cement	6.0% cement
20 Before impact	13.0 cm	15.0 cm
After impact	18.5 cm	19.7 cm

25 Four cylinders (200 mm x 100 mm diameter) were prepared from each mixture.

The samples were hardened at 80°C in sealed forms in water for 24 hours and then at 20°C in sealed forms for 24 hours, followed by 5 days at 20°C in air.

30 The weight loss after storage for 5 days in air at 20°C was as follows:

C-6%:	0.28%
C-12.5%:	0.13%

The cylinders were tested for density, sound velocity, dynamic modulus of elasticity and compressive strength as described above. Density, sound velocity and dynamic modulus of elasticity was determined immediately after removal from the molds, while
 5 compressive strength was determined after another 5 days. The results were as follows:

Mixture	12.5% cement	6.0% cement
Density (kg/m ³)	2303	2279
10	(3)	(3)
Sound velocity (m/sec.)	5128	4711
	(28.3)	(11.1)
E-Dynamic (MPa)	60,583	50,589
15	(729)	(289)
Compressive strength (MPa)	108	61
	(1.0)	(3.7)

The results show the improvement in quality obtained when using the
 20 fine cement instead of the cement with larger particle size. Thus, the compressive strengths of the specimens with the fine cement are 28% and 57%, respectively, higher than the corresponding specimens with the larger cement particles. Also the stiffness is improved considerably, as appears from the increased values of the dynamic
 25 modulus of elasticity. It should be noted that the percentage quality improvement is largest at the lower cement content, indicating the possibility of producing satisfactory materials having still lower cement content.

EXAMPLE 3

Preparation of mortars with various materials as the fine, inactive particles

- 5 A great number of materials are useful as the fine, inactive particles C. One such type of material is ground quartz. A mortar with ground quartz as particles C can be prepared as follows:

Mix composition:

		g per approx. 10 l mortar		
		C-25%	C-12.5%	C-6%
10	White cement*	1935	965	465
	Silica	1845	1845	1845
	Quartz*	4658	5434	5840
	Flube	235	235	235
15	Sand 0-0.25 mm	1980	1980	1980
	Sand 0.25-1 mm	3945	3945	3945
	Sand 1-4 mm	7895	7895	7895
	Water	1285	1285	1285

- 20 * Finely ground, such as very fine white cement I

Production and testing is carried out in the same manner as in Example 2.

Mortars may also be prepared according to the following mixes, which contain various materials as the fine, inactive particles C.

	Mix ref.	Mix 1	Mix 2	Mix 3	Mix 4
White cement*	3880	3880	3880	3880	3880
Microsilica	3700			3700	3700
5 Precipited CaCO ₃			4320		
Fine Al ₂ O ₃		5980			
Flyash III	8180	8180	8180		
Flyash C					9770
Slag				10500	
10 Flube	460	460	460	460	460
Sand 0-0.25 mm	3960	3960	3960	3960	3960
Sand 0.25-1 mm	7900	7900	7900	7900	7900
Sand 1-4 mm	15800	15800	15800	15800	15800
Water	2580	2580	2980	2580	4100
15					
	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9
White cement*	3880	3880	3880	3880	
Rapid cement					3880
20 Microsilica	3700	3700	3700	3700	3700
Precipited CaCO ₃					
Fine Al ₂ O ₃					8180
Flyash F	7900				
Greek dolomite		10040			
25 Norwegian dolomite			10040		
Calcite filler				9680	
Flube	460	460	460	460	460
Sand 0-0.25 mm	3960	3960	3960	3960	3960
Sand 0.25-1 mm	7900	7900	7900	7900	7900
30 Sand 1-4 mm	15800	15800	15800	15800	15800
Water	2580	2840	2840	2840	2580

Precipitated CaCO₃: average particle size 0.7 μm , surface area 23 m^2/g

- Fine Al_2O_3 : average particle size $0.5 \mu\text{m}$, specific surface (BET) $3.5 \text{ m}^2/\text{g}$
- Greek dolomite: $99\% < 50 \mu\text{m}$, $53\% < 10 \mu\text{m}$, $11\% < 1 \mu\text{m}$, density 2875 kg/m^3
- 5 Norwegian dolomite: average particle size $15 \mu\text{m}$, $98\% < 70 \mu\text{m}$, specific surface is (BET) $1 \text{ m}^2/\text{g}$
- Calcite filler: $98\% < 50 \mu\text{m}$, $59\% < 10 \mu\text{m}$, $16\% < 1 \mu\text{m}$, density 2755 kg/m^3
- Slag: Blaine surface $326 \text{ m}^2/\text{kg}$, density 2930 kg/m^3
- 10 Fly ash C: $97\% < 50 \mu\text{m}$, $58\% < 10 \mu\text{m}$, $4\% < 1 \mu\text{m}$, density 2203 kg/m^3
- Fly ash F: $76\% < 63 \mu\text{m}$, $47\% < 20 \mu\text{m}$, $16\% < 10 \mu\text{m}$, $1\% < 2 \mu\text{m}$, density 2726 kg/m^3

EXAMPLE 4

15 *Preparation of concrete*

A concrete with a fine mortar and a high concentration of irregularly shaped stone (5-11 mm) can be prepared as follows:

The fine mortar comprises the same binder material as in Example 2, (C-25%).

20 The mix composition is as follows:

	Grams	
	White cement*	1935
	Silica	1845
	Fly ash	4085
25	Flube	235
	Sand 0-0.25 mm	5067
	Sand 0.25-1.0 mm	10133
	Stone 5-8 mm	8430
	Stone 8-11 mm	23555
30	Water	1285

* Finely ground, such as very fine white cement I

Samples are produced as described above in "Materials and Methods" by mixing in a 50 l paddle blender in a two-step process, i.e. first the mortar is mixed, after which (after addition of the stone) the concrete is mixed.

- 5 A flow table measurement is performed on the mortar as described above.

Cylinders (200 mm x 100 mm diameter) are prepared by casting using a vibration of 150 cycles per second with a counterweight, as described above.

10 EXAMPLE 5

Mortars with finely ground cement and finely ground fly ash

- Materials (mortar) comprising about 25% by volume of cement and about 75% by volume of fly ash with a "normal fineness" to which finely ground fly ash (with a particle size about half that of normal fly ash) had been added were prepared. The finely ground cement was the same as in Example 2.
- 15

The mortar was a "standard mortar" with the same sand composition as in Example 1 and with the same volume of binder powder. The water content was in this case about 20% greater.

- 20 The mix composition was as follows:

37

Grams

	Normal fly ash	3987
5	Finely ground fly ash	2375
	Finely ground white cement	1935
	Flube	235
10	Quartz sand	
	0-0.25 mm	1980
	0.25-1 mm	3945
	1.0-4.0 mm	7895
	Water	1400

- 15 Mixing and casting took place as described in Example 1 and in "Materials and Methods".

Flow table measurements gave values of 14.5 cm before impact and 19.0 cm after impact.

Six cylinders (200 mm x 100 mm diameter) were prepared.

- 20 Hardening was as follows:

- 1) 3 cylinders were hardened with heat in sealed molds for 18 hours at about 45°C and then for 24 hours at 80°C, followed by 24 hours at 20°C, after which time the cylinders were removed from the molds. The cylinders were then kept dry at 20°C for 6 days. The weight loss
25 after storage for 6 days at 20°C in air was 0.11%.

- 2) 3 cylinders were stored for 2 days in sealed molds in water with a temperature of 20°C, followed by removal from the molds and storage in water at 20°C for 13 days and then for 6 days at 45°C in air. The weight increase after 13 days of storage in water was 0.48%. The
30 weight loss after storage for 6 days in air at 45°C was 0.86%.

Density, sound velocity, dynamic modulus of elasticity and compressive strength were determined as described above. The results are summarized in the following table:

		20°C 2 days	20°C 13 days	80°C
	Density (kg/m ³)	2341 (4.6)	2352 (3.5)	2333 (4.0)
5	Sound Velocity (m/sec.)	4736 (13.0)	5277 (0.0)	5310 (8.1)
	E-Dynamic (MPa)	52500 (371.8)	65505 (97.9)	65766 (277.1)
10	Compressive strength (MPa)	-	109.9* (1.1)	110.6 (9.3)

* After an additional 6 days at 45°C

EXAMPLE 6

Mortar with bauxite as the fine aggregate

Three mortars having relative mix compositions substantially
 15 identical to mixes C-25%, C-12.5%, and C-6% of Example 1, with the
 exception that the quartz sand is replaced by bauxite, the 0-0.25 mm
 and 0.25-1 mm quartz sand fractions being replaced by a 0-1 mm
 bauxite fraction on a volume to volume basis, and the 1-4 mm quartz
 sand being replaced by a 1-4 mm bauxite fraction, likewise on a
 20 volume to volume basis, can be prepared as follows:

The total volume (sum of the dry constituent components + water) of
 the mixes is 35 litres.

The mix compositions (in grams) are as follows:

	C-25%	C-12.5%	C-6%
White Portland cement*	6773	3378	1628
5 Microsilica II	6458	6458	6458
Fly ash III	14,298	16,678	17,924
Flube	823	823	823
Bauxite 0-1 mm	25,043	25,043	25,043
Bauxite 1-4 mm	33,370	33,370	33,370
10 Water	4498	4498	4498
Theoretical densities (g/cm ³)			
	2.697	2.667	2.652
15 *Finely ground, such as very fine white cement II			

Mixing is carried out according to the procedure described in "Materials and Methods" using a 50 litre mixer.

The consistency of the mixed materials prior to casting is determined by flow table measurements as described in "Materials and Methods".

- 20 From each mix, a series of cylindrical samples (200 mm x 100 mm in diameter) is prepared by casting using a vibration of 150 cycles per second with a counterweight, as described above.

EXAMPLE 7

Concrete with steel powder and bauxite

- 25 Concrete cylinders using steel powder and bauxite may be prepared as follows:

Cylinders (200 mm x 100 mm diameter) are cast, cured at 20°C and 100% relative humidity for 48 hours and removed from the molds.

The cylinders are cast from the following mix:

40

	White cement*	7724 g
	Microsilica II	7377 g
	Steel powder	42,521 g
	Flube	931 g
5	Bauxite 0-1 mm	25,903 g
	Bauxite 1-4 mm	34,520 g
	Water	5631 g

*Finely ground, such as very fine white cement II

10 The steel powder has a density of 7628 kg/m^3 and the following particle size distribution:

	<500 μm	100%
	<250 μm	99%
	<125 μm	97%
	<106 μm	96%
15	<90 μm	78%
	<75 μm	73%
	<63 μm	55%
	<38 μm	27%

The other materials are the same as those used in Example 6.

20 EXAMPLE 8

Reference example. Mortar with aluminous cement

A mortar was prepared having a relative mix compositions identical to mix C-6% of Example 6, with the exception that the white Portland cement was replaced by a refractory high alumina cement (Alcoa CA-14)
25 on a volume for volume basis. The mix composition was as follows:

41

C-6%

	High alumina cement	1540
	Microsilica II	6458
	Fly ash III	17,924
5	Flube	823
	Bauxite 0-1 mm	25,043
	Bauxite 1-4 mm	33,370
	Water	4498

- Mixing was carried out according to the procedure described in
- 10 "Materials and Methods" using a 50 litre mixer.

The consistency of the mixed material prior to casting was determined by flow table measurements as described in "Materials and Methods". The results are as follows (see Example 2 for explanation).

C-6%

15	Before	12.5
	After	18.0

- From the mix, a series of cylindrical samples (200 mm x 100 mm in diameter) was prepared. After casting, the sealed molds were cured at 20°C (wrapped in water-soaked towels and sealed in plastic bags) for
- 20 6 days, after which the samples were removed from the molds. The setting times ranged from 1 to 2 days. Density, sound velocity and dynamic modulus of elasticity were determined as described in "Materials and Methods". The results are given below.

42

C-6%

	Density (kg/m ³)	2663 (14)
5	Sound velocity (m/s)	3880 (40)
	E-dynamic (MPa)	39,890 (920)

The samples were then submerged in water at 20°C and cured until 28 days had elapsed since initial casting. After 28 days, 3 samples from each series were removed and the density, sound velocity and dynamic modulus of elasticity were determined. The samples were then dried for 5 days at 45°C, after which the compressive strength was determined. The results are given below.

After 28 days of curing in water at 20°C

15		C-6%
	Density (kg/m ³)	2674 (7)
	Sound velocity (m/s)	4220 (40)
20	E-dynamic (MPa)	47,630 (1050)

*After 28 days of curing in water at 20°C
+ 5 days of drying at 45°C*

25	Compressive strength (MPa)	22.3 (0.6)
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EXAMPLE 9

Mortar with finely ground aluminous cement and bauxite

Using the aluminous cement of Example 8 which had been finely ground to give the particle size distribution listed under "Materials and
5 Methods", 18 cylinders (200 mm x 100 mm in diameter) were cast. It was noted that a relatively long mixing time was required before the dry mix acquired a plastic consistency. The composition of the mix was as follows (6% by volume cement, based on cement + fly ash):

	Fine aluminous cement	1540 g
10	Microsilica II	6458 g
	Fly ash III	17,924 g
	Flube	823 g
	Bauxite 0-1 mm	25,043 g
	Bauxite 1-4 mm	33,370 g
15	Water	4498 g

The cylinders were hardened at 20°C and 100% relative humidity for 24 hours, after which the molds were removed and the density and dynamic modulus of elasticity were determined. The following results were obtained (standard deviations in brackets):

20	Density (kg/m ³)	2692 (16)
	E-dynamic (MPa)	41,800 (1490)

Three cylinders were further cured in water at 20°C for 30 days,
25 after which the following results for density and dynamic modulus of elasticity were obtained:

	Density (kg/m ³)	2708 (21)
30	E-dynamic (MPa)	55,130 (1610)

These cylinders were then dried for 5 days at 45°C, after which the following results for density, dynamic modulus of elasticity and compressive strength were obtained:

5	Density (kg/m ³)	2627 (21)
	E-dynamic (MPa)	51,610 (1500)
	Compressive strength (MPa)	36.6 (0.3)

10 EXAMPLE 10

Materials with an extremely low cement content

Concrete having an extremely low cement content may be prepared and cast using binders based on very fine white Portland cement, fly ash and microsilica with a volume ratio between cement and cement plus fly ash of 6%, 3% and 1.5%, respectively, and a microsilica content of about 25% based on the total powder volume. The concrete may also contain quartz sand with a size of 0-1 mm and hyperite stone with a size of 5-11 mm. The recipes (weight in g) for the mixes (about 34 l each) are as follows.

20		6%	3%	1.5%
	White Portland cement*	820	420	205
	Fly ash	9282	9578	9726
	Microsilica	3322	3322	3322
25	Flube	336	336	336
	Sand 0-0.25 mm	9000	9000	9000
	Sand 0.25-1 mm	18,000	18,000	18,000
	Water	2515	2515	2515
	Hyperite 5-8 mm	14400	14400	14400
30	Hyperite 8-11 mm	32400	32400	32400

*Finely ground, such as very fine white cement II

The concrete may be prepared as described in Example 4. From each batch, 18 cylinders (20 cm x 10 cm diameter) may be cured as follows.

Curing No.

- 1 in water at 20°C for 28 days after casting;
 - 5 2 in water at 20°C for 28 days after casting plus 5 days at 45°C in air;
 - 3 in water at 20°C for about 7 months;
 - 4 in water at 20°C for about 7 months plus 5 days at 45°C in air.
- 10 It is expected that excellent compressive strength values may be obtained in such materials using a combination of 1) a low amount of a finely ground cement, and 2) relatively long curing times.

EXAMPLE 11

15 *Dense fine material prepared using moderate vibration and pressure compaction*

The fine components of the fine materials, i.e. microsilica (0.2 μm), cement (15 μm) and fly ash (15 μm), are uniformly premixed with water and an effective dispersing agent to form a viscous mass with a high particle concentration of about 0.70, corresponding to water
20 saturation just being achieved during the mixing process. The "coarse" component of the fine materials, i.e. very fine quartz sand (average particle size 80 μm), is then added in increasing amounts. The amount of liquid is now too little to saturate the materials during mixing, due to the increase in the amount of particles. During
25 mixing, the material now obtains an earthy to dry, lumpy to grainy consistency. Small samples of the material are taken and compressed using light to moderate vibration and pressure compaction, whereby the particle system is packed so that the voids are significantly reduced, so that liquid saturation is achieved.

30 Thus, fine materials in which the particle concentration (A + B + C, C being the fraction of the fine sand below 100 μm) is increased from

about 0.70 to about 0.82 may be prepared using a process in which 1) the essential homogenous distribution of all of the fine components and the liquid are achieved using fluid-mixing in a saturated state, 2) a relatively homogenous distribution of the coarse components is achieved by long and thorough intermixing in a powder mass having a plastic to lumpy consistency, and 3) the final, dense particle packing is achieved using vibration and pressure compaction without pressing excess water out of the material, which is required to achieve similar density if the entire mixing process (using more liquid) is to take place at one time in a water saturated condition.

MATERIALS

White Portland cement, fly ash, microsilica, and Flube corresponding to that which is described for the previous examples may be used. The employed fine quartz sand particles has a size in the range of 0-0.125 mm and an average size of 80 μ m.

The mix compositions (g) are shown in the following table.

Mix No.	1	2	3	4	5
White Portland cement*	414	414	414	414	414
Microsilica	395	395	395	395	395
Fly ash	875	875	875	875	875
Flube	50	50	50	50	50
Water	275	275	275	275	275
Quartz sand 0-0.125 mm	0	1500	1750	2000	2250

*Finely ground, such as very fine white cement II

The composition of the materials without the quartz sand is substantially as given in Example 1 (C-25), with the exception that the amounts are smaller.

Mixing may e.g. take place in a Hobart mixer. The fine materials, i.e. cement, fly ash, microsilica and Flube, are dry-mixed for 1

min., after which all the water is added and mixing is continued for another 10 min., followed by further addition of fine sand (see the table with the mix compositions) using a total mixing time of about 45 min.

- 5 The consistency may be determined visually based on 1) the characteristics of the mixes during mixing, and 2) samples of the mixes, using light to moderate vibration and pressure compaction.

- 10 For the determination of consistency small samples of materials with different sand contents in sealed plastic bags may be placed on a vibrator table and vibrated for 20-30 sec. using a metal weight during vibration to press the samples into flat discs with an area of about 10-20 cm².

Vibration frequency: 50 Hz; acceleration about 100 m/s²
Weights: about 200 g, 500 g, 8000 g.

15 EXAMPLE 12

Materials prepared with fine narrowly graded and extremely dense binders

- 20 In this example the following materials are prepared: 1) fine binders with a maximum particle size of about 12 μm and showing a combination of good fluidity and density, and 2) extremely dense binders prepared by adding fine sand (63-90 μm) to the fine binders. The binders were tested in a quartz sand mortar.

MATERIALS

- 25 Cement: air-classified white Portland cement with a narrow particle size distribution and a small particle size (average size 5 μm and substantially all of the particles between 2 and 10 μm), density 3150 kg/m³. The following values were determined for the distribution of the cement particles (with reference

to the definitions given in the specification): $D_{90} = 8.0 \mu\text{m}$, $D_{50} = 4.8 \mu\text{m}$, $D_{10} = 2.6 \mu\text{m}$, $D_5 = 2.0 \mu\text{m}$.

5 Fly ash: air-classified fly ash with a narrow particle distribution and a small particle size (average size $6 \mu\text{m}$ and substantially all of the particles between 2 and $12 \mu\text{m}$), density 2320 kg/m^3 . The following values were determined for the distribution of the cement particles (with reference to the definitions given in the specification): $D_{90} = 12.5 \mu\text{m}$, $D_{50} = 6.4 \mu\text{m}$, $D_{10} = 3.15 \mu\text{m}$, $D_5 = 2.65 \mu\text{m}$.

10 Microsilica: as in Example 1.

Dispersing agent: Flube

15 Sieved fine sand ("Sæby sand"): rounded quartz sand with a particle size between $63 \mu\text{m}$ and $90 \mu\text{m}$, density about 2600 kg/m^3 .

Quartz sand: $0.25\text{-}1 \text{ mm}$ and $1\text{-}4 \text{ mm}$ (as in Example 2).

The mix compositions (in g) are as follows.

49

		Mix No.			
Mortars with fine binders		I	II	III	IV
5	Cement	213	213	213	213
	Fly ash	470	470	470	470
	Microsilica	200	200	200	200
	Disp. agent	24	24	24	24
	Water	130	135	140	150
10	Sand 0.25-1 mm	333	333	333	333
	Sand 1-4 mm	667	667	667	667

Mortar with dense binder - Mix V

- 15 Fine mortar IV plus 750 g fine sand (63-90 μ m).
The following values were determined for the mixes:

		Mix No.				
		I	II	III	IV	V
20	B					
	B + C	0.25	0.25	0.25	0.25	0.121
25	A					
	A+B+C	0.25	0.25	0.25	0.25	0.139
	A+B+C in binder	0.713	0.706	0.699	0.686	0.797*

- 30 * It is expected that a value of about 0.90 may be obtained using vibration and pressure compaction.

PREPARATION OF THE MIXES AND DETERMINATION OF FLUIDITY

- The dry materials for the fine mortar (everything except the water) were mixed for 1 min. in a Hobart mixer. The water was then added,
35 first 120 g and then gradually to 130 g, and mixing was carried out

for 5-10 min. Flow measurements were then made, after which another 5 g of water was added and mixing was carried out for another 5-10 min., followed by flow measurements for this mix (mix II). The same procedure was used for mixes III and IV. 750 g of fine sand (63-90 μm) were then added and mixing was carried out for another 5-10 min., after which 6 cylinders (9 cm x 4.5 cm diameter) were cast using vibration (50 Hz, acceleration about 50-100 m/s^2) with a light counterweight. The samples were hardened for about 60 hours in water at 80°C in sealed moulds. The samples were then removed from the moulds and after cooling to 20°C density, sound velocity and compressive strength were determined. The results of the flow measurements are given below.

Mix	Flow measurement (cm)		Volume concentration	
	static	dynamic	solid	liquid
I	10.3	13.7	0.713	0.287
II	10.7	15.0	0.706	0.294
III	10.9	16.0	0.699	0.301
IV	15.7	20.3	0.686	0.314
V	plastic		0.797	0.203

The mixing and measurement of fluidity for mixes I, II, III and IV and mixing of mix V took a total of a little more than 1 hour, during which the temperature of the material increased from about 20°C to 30°C during the mixing of mix V.

This somewhat unusual procedure has undoubtedly resulted in a slightly poorer fluidity than one would achieve using a "normal procedure" with, for example, mixing of the fine mortar (mix IV) for 10-15 min. and subsequent addition of fine sand and mixing of the dense mortar (mix V) for a further 5-10 min., i.e. a total mixing time of about 20 min.

The results of the measurements on the hardened cylinders are given below.

	Density* kg/m ³	Sound velocity* m/sec.	Dynamic modulus* of elasticity MPa	Compressive strength** MPa
5	2330	5005	58,359	175,7
	(63)	(32.7)		(19,7)

* determined for 6 samples

** determined for 3 samples

10 COMMENTS

The density of 2330 kg/m³ indicates that the desired extremely dense packing has been achieved, since the theoretical density, under the assumption of 0% air and calculated on the basis of the density of the individual components and the mixing ratio, is 2352 kg/m³. This indicates that the material contains only about 1% trapped air. The results of the compressive strength measurements indicate that these are completely unique materials, especially seen in the light of the fact that 1) the ratio B/(C+B) is only 12%, and 2) the mortar was prepared using normal quartz sand and not particularly strong sand.

The fine binder of mixes I-IV shows a low maximum particle size of 12 µm and a very dense packing of the particles A, B, and C, corresponding to a water/cement ratio by weight of about 0.11-0.13 if all particles are calculated as having cement density and ignoring the dispersing agent, in other words in accordance with the calculations in concrete technology. The fine binder also shows a high fluidity, as evidenced by the most dense of the materials being easily castable under vibration, and the other materials being almost self-levelling.

The fine binder material shows an excellent performance, as appears from the results obtained with Mix V, where the fine binder was combined with the very narrowly graded fine sand particles. This indicates that the fine binder would be very useful as a binder in e.g. fine components composites, such as composites using 5-15 µm

diameter fibres in high volume concentration, to result in materials of very high quality.

The dense binder of mix V shows very excellent properties which would not have been expected to be obtainable in such a material cast with conventional vibration technique. The properties are especially remarkable in view of the fact that the mortar in which the binder is tested is a quartz sand mortar. Still better properties are to be expected when the binder is used in a mortar with strong sand particles such as calcined bauxite. Also, the binder shows a high content, 57% by volume, of particles C, demonstrating the potential of the materials of the present invention in connection with the utilisation of particles C which have special properties, such as magnetic particles or wear resistant particles.

This example, compared with Example 2, demonstrates the effect of the preferred use of the narrowly graded cement and the narrowly graded fine particles C (in mix V together with narrowly graded larger particles C), and indicates that excellent materials may be obtained even with very low cement contents in such materials, such as 6%, 3%, and 1% by volume. Finally, the example indicates that still better properties must be expected when these materials are combined, by vibrational compaction, with still higher amounts of the narrowly graded sand, compare the teaching of Example 11.

EXAMPLE 13

Experiments were carried out on mortars to illustrate the effect of 1) the water requirement necessary to achieve a given flow behaviour, and 2) the flow behaviour of various factors such as the fineness and particle size distribution of the cement.

The fundamental behaviour with respect to fluidity and water requirement has been shown to be the same regardless of whether all of the fine articles are cement particles or only a fraction of the fine particles are cement particles and the remainder are inactive fine particles. Of course, the numerical values will reflect the total amount of fine particles and the particle size distribution as

well as the shape of the inactive fine particles. Furthermore, these experiments are related to compatibility tests which may be carried out for the determination of the physical and chemical compatibility of a given combination of cement, ultrafine particles, and dispersing agent.

In the experiments, the individual mortars were first mixed using a certain amount of water, after which the amount of water was gradually increased and the consistency and flow behaviour of the mix was observed and measured. The consistency was determined as described in materials and methods, i.e. using the ASTM C230-83 standard for flow table measurements. The materials of the various mixes are also described in the Materials and Methods section.

Mixing took place in a Hobart mixer. The dry ingredients (including the dispersing agent (Flube, which was in powder form) were first mixed for one minute. Water was subsequently added. The materials were then mixed, and the consistency was determined visually. Water was subsequently added at intervals of about 2-5 minutes, and the behaviour of the mixes was recorded, including when the mix changed from a damp, lumpy condition to a plastic condition. After this change, more water was added, and the flow behaviour of the mix was determined after each new addition of water. Furthermore, the volume amount of liquid in the binder as well as the volume amount of powder in the binder was determined. The compositions of the mixes as well as the results of the experiments are shown below.

Mix No.	1	2
Sæby sand	1000	750
5 Fine white Portland cement	800	
Air-classified fine white cement		600
Microsilica	200	150
Flube	24	18
10		

	Mix No.	Time (min.)	Water g	Flow measurement (cm)		Liquid in binder	A+B+C in binder	Comments
				Static	Dynamic			
15	1	5	190	10.0	13.2	0.395	0.605	change (6 min.) to plast.con.
		12	210	10.3	15.3	0.416	0.584	
		17	230	10.7	17.7	0.435	0.565	
20			250	11.6	19.5	0.453	0.547	
	2	4	130					
		7	140					change to plast. con.
		9	150	14.5	20.5	0.385	0.615	very flow-ing
25								

This example shows the effect of replacing fine white Portland cement having a "normal" particle size distribution with a graded (air-classified) fine white Portland cement having a narrow particle size distribution, the water requirement of the mix containing the latter being significantly lower than that of the mix containing the former.

CLAIMS

1. A shaped article comprising a cement-bound matrix comprising
 - A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, the particles having an average size in the range of 0.002-2 μm ,
 - B) cement particles having an average size in the range of 2-7 μm ,
 - C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, the particles C having an average size in the range of 3-100 μm , the maximum size of the particles being 100 μm ,
 - D) a dispersing agent in an amount of 0.1-4% by weight of dry matter, calculated on the total weight of the particles A+B+C,

the amount by volume of the particles B being in the range of 0.01-0.40 times the total volume of the particles B+C,
- 15 the volume ratio of A based on the total volume of A+B+C being in the range of 0.10-0.40, and
- the volume concentration of A+B+C in the matrix being at least about 0.55.
2. A shaped article according to claim 1, wherein the amount by volume of the cement particles is in the range of 0.20-0.40, based on B+C.
3. A shaped article according to claim 1, wherein the amount by volume of the cement particles is in the range of 0.10-0.20, based on B+C.
- 25 4. A shaped article according to claim 1, wherein the amount by volume of the cement particles is in the range of 0.01-0.10, based on B+C.

5. A shaped article according to any of the preceding claims wherein the cement particles have an average size in the range of 2-5 μm .
6. A shaped article according to any of the preceding claims wherein the cement particles have a narrow particle size distribution with the ratio D_{90}/D_{10} being at the most about 12.
7. A shaped article according to claim 6 wherein the ratio D_{90}/D_{10} of the cement particles is in the range of 3-10.
8. A shaped article according to claim 6 or 7 wherein the ratio D_{10}/D_5 of the cement particles is at the most 1.5.
- 10 9. A shaped article according to any of the preceding claims wherein the particles A have an average size in the range of 0.03-1 μm .
10. A shaped article according to any of the preceding claims wherein the particles A have an average size of about 0.1-0.5 μm .
11. A shaped article according to any of the preceding claims wherein the particles C have an average size in the range of 50-100 μm .
12. A shaped article according to any of the preceding claims wherein the particles C have an average size in the range of 2-20 μm .
13. A shaped article according to claim 11 or 12 wherein the particles C have a narrow size distribution with the ratio D_{90}/D_{10} being at the most about 10.
14. A shaped article according to claim 13 wherein the particles C have a ratio D_{90}/D_{10} of at the most about 6.
15. A shaped article according to any of claims 1-10, wherein the particles C comprise two fractions with gap grading, one fraction having an average size in the range of 50-100 μm , the other fraction having an average size in the range of 2-10 μm .

16. A shaped article according to claim 15, wherein one or both of the particle C fractions has/have a narrow particle size distribution, the ratio D_{90}/D_{10} of the fraction having an average size in the range of 50-100 μm being at the most 4, and/or the ratio
5 D_{90}/D_{10} of the fraction having an average size in the range of 2-10 μm being at the most about 8.

17. A shaped article according to any of the preceding claims wherein the particles C are substantially spherical.

18. A shaped article according to any of the preceding claims wherein
10 the average size of the particles C is at least 3 times the average size of the particles A.

19. A shaped article according to any of the preceding claims wherein the average size of the particles C is at least 10 times the average size of the particles A.

15 20. A shaped article according to any of the preceding claims wherein the average size of the particles C is at least about 100 times the average size of the particles A.

21. A shaped article according to any of the preceding claims wherein the cement particles B are chosen from the group consisting of normal
20 Portland cement, high early strength Portland cement, white Portland cement, Portland blast furnace cement, Portland pozzolana cement, low-alkali cement, fly ash cement, sulfate resistant cement and alumina cement.

22. A shaped article according to any of the preceding claims wherein
25 the particles A are chosen from the group consisting of alumina, calcium carbonate, calcium hydroxide, rice husk ash, metakaolin, oxides such as SiO_2 , zirconium oxide and titanium oxide, and ground and/or sieved fly ash, quartz and slag.

25. A shaped article according to claim 22 wherein the particles A
30 comprise microsilica from the production of ferrosilicium or silicon metal.

26. A shaped article according to any of the preceding claims wherein the particles C are chosen from the group consisting of fly ash, fine quartz sand, slag, alumina, calcium carbonate and calcium carbonate-containing minerals such as dolomite and calcite, metakaolin, metal particles such as steel powder, and oxides such as Al_2O_3 , SiO_2 , zirconium oxide, titanium oxide, and refractory grade bauxite.

27. A shaped article according to any of the preceding claims in which the volume concentration of A+B+C in the matrix is at least 0.60.

28. A shaped article according to claim 27 in which the volume concentration of A+B+C in the matrix is at least 0.70.

29. A shaped article according to claim 25 in which the volume concentration of A+B+C in the matrix is at least 0.75.

30. A cement-containing powder composition comprising

A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, the particles having an average size in the range of 0.002-2 μm ,

B) cement particles having an average size in the range of 2-7 μm , and

C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, the particles C having an average size in the range of 3-100 μm , the maximum size of the particles being 100 μm ,

the amount by volume of the particles B being in the range of 0.01-0.40 times the total volume of the particles B+C, and

the volume ratio of A based on the total volume of A+B+C being in the range of 0.10-0.40.

31. A cement-containing powder composition capable of forming a binder matrix by mixing with water and curing, comprising

A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, the particles having an average size in the range of 0.002-2 μm ,

B) cement particles having an average size in the range of 2-7 μm ,

C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, the particles C having an average size in the range of 3-100 μm , the maximum size of the particles being 100 μm , and

D) a dispersing agent in an amount of 0.1-4% by weight of dry matter, calculated on the total weight of the particles A+B+C,

the amount by volume of the particles B being in the range of 0.01-0.40 times the total volume of the particles B+C, and

the volume ratio of A based on the total volume of A+B+C being in the range of 0.10-0.40.

32. A powder composition according to claim 31 or 32 which additionally comprises sand having an average particle size of 0.2-4 mm in an amount of 0.3-3 times the volume of the particles A+B+C.

33. A powder composition according to any of claims 30-32, wherein the amount by volume of the cement particles is in the range of 0.20-0.40.

34. A powder composition according to any of claims 30-32, wherein the amount by volume of the cement particles is in the range of 0.10-0.20.

35. A powder composition according to any of claims 30-32, wherein the amount by volume of the cement particles is in the range of 0.01-0.10.

36. A powder composition according to any of claims 30-35, wherein the cement particles have an average size in the range of 2-5 μm .
37. A powder composition according to any of claims 30-36, wherein the cement particles have a narrow particle size distribution with the ratio D_{90}/D_{10} being at the most about 12.
38. A powder composition according to claim 37, wherein the ratio D_{90}/D_{10} of the cement particles is in the range of 3-10.
39. A powder composition according to claim 37 or 38 wherein the ratio D_{10}/D_5 of the cement particles is at the most 1.5.
40. A powder composition according to any of claims 30-39 wherein the particles A have an average size in the range of 0.03-1 μm .
41. A powder composition according to any of claims 30-40 wherein the particles C have an average size in the range of 50-100 μm .
42. A powder composition according to any of claims 30-40 wherein the particles C have an average size in the range of 2-20 μm .
43. A powder composition according to claim 41 or 42 wherein the particles C have a narrow size distribution with the ratio D_{90}/D_{10} being at the most about 10.
44. A powder composition according to claim 43 wherein the particles C have a ratio D_{90}/D_{10} of at the most about 6.
45. A powder composition according to any of claims 30-40, wherein the particles C comprise two fractions with gap grading, one fraction having an average size in the range of 50-100 μm , the other fraction having an average size in the range of 2-10 μm .
46. A powder composition according to claim 45, wherein one or both of the particle C fractions has/have a narrow particle size distribution with the ratio D_{90}/D_{10} of the fraction having an average

size in the range of 50-100 μm being at the most 4, and/or the ratio D_{90}/D_{10} of the fraction having an average size in the range of 2-10 μm being at the most about 8.

47. A powder composition according to any of claims 30-46 wherein the particles C are substantially spherical.

48. A powder composition according to any of claims 30-47 wherein the cement particles B are chosen from the group consisting of normal Portland cement, high early strength Portland cement, white Portland cement, Portland blast furnace cement, Portland pozzolana cement, low-alkali cement, fly ash cement, sulfate resistant cement and alumina cement.

49. A powder composition according to any of claims 30-48 wherein the particles A are chosen from the group consisting of alumina, calcium carbonate, calcium hydroxide, rice husk ash, metakaolin, oxides such as SiO_2 , zirconium oxide and titanium oxide, and ground and/or sieved fly ash, quartz and slag.

50. A powder composition according to any of claims 30-48 wherein the particles A comprise microsilica (ultrafine silica fume) from the production of ferrosilicium or silicon metal.

51. A powder composition according to any of claims 1-50 wherein the particles C are chosen from the group consisting of fly ash, fine quartz sand, slag, alumina, calcium carbonate and calcium carbonate-containing minerals such as dolomite and calcite, metakaolin, metal particles such as steel powder, and oxides such as Al_2O_3 , SiO_2 , zirconium oxide, titanium oxide, and refractory grade bauxite.

52. A fluid composition comprising the constituents as defined in any of claims 30-51, and water.

53. A fluid composition according to claim 52, wherein the water is present in an amount not exceeding the amount which will allow a

volume concentration of the particles A+B+C of at least 0.55 in a matrix made from the composition.

54. A powder composition comprising for producing a binder matrix by mixing with cement, a dispersing agent and water and curing,
5 comprising

A) inorganic solid particles which are inactive or substantially less active than cement with respect to solidification of the matrix, the particles having an average size in the range of 0.002-2 μm ,

- 10 C) inorganic solid particles which are inactive or substantially less active than the cement particles B with respect to solidification of the matrix, the particles C comprising two fractions with gap grading, one fraction having an average size in the range of 50-100 μm , the other fraction having an average size in the range of 2-10 μm .

- 15 55. A powder composition according to claim 54, wherein one or both of the particle C fractions has/have a narrow particle size distribution with the ratio D_{90}/D_{10} of the fraction having an average size in the range of 50-100 μm being at the most 4, and/or the ratio D_{90}/D_{10} of the fraction having an average size in the range of 2-10
20 μm being at the most about 8.

56. A powder composition according to claim 54 or 55 which additionally contains a dispersing agent.

57. A liquid composition comprising the constituents as defined in any of claims 54-56 and water.

- 25 58. A shaped article as according to any of claims 1-29 or a compositiona according to any of claims 30-57 wherein the cement is white Portland cement or low alkali cement.

INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 90/00113

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 04 B 28/02, 18/06		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 04 B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A1, 0010777 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 14 May 1980, see the whole document --	1-58
A	EP, A1, 0042935 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 6 January 1982, see the whole document --	1-58
A	EP, A2, 0067456 (DANSK ETERNIT-FABRIK A.S.) 22 December 1982, see the whole document --	1-58
A	US, A, 4504320 (JANINE M. RIZER ET AL) 12 March 1985, see the whole document -- -----	1-58
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
27th July 1990	1990 -08- 0 1	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	May Hallne <i>May Hallne</i>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 90/00113**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on **90-05-24**.
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0010777	80-05-14	AU-B- 538813	84-08-30
		AU-D- 5250979	80-05-15
		CA-A- 1190947	85-07-23
		WO-A- 80/00959	80-05-15
EP-A1- 0042935	82-01-06	AU-D- 7078781	81-11-26
		CA-A- 1197269	85-11-26
		DE-A- 3176917	88-12-01
		US-A- 4588443	86-05-13
		WO-A- 81/03170	81-11-12
EP-A2- 0067456	82-12-22	CA-A- 1205828	86-06-10
		EP-A-B- 0165388	85-12-27
		US-A- 4636345	87-01-13
US-A- 4504320	85-03-12	NONE	